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SIMPLIFIED RATE-LAW INTEGRATION FOR REACTANTS WHICH ARE FIRST ORDER IN EACH OF TWO REACTANTS

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The purpose of this paper is to present a simple procedure for integrating the rate law for chemical reactions which are first order in each of two reactants.

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If a chemical reaction involving two reactants, $aA + bB \rightarrow \text{products}$, is first order in each of its two reactants (and second order overall) then it follows the rate law

$$-\frac{d[A]}{a \, dt} = -\frac{d[B]}{b \, dt} = k[A][B] \quad (1)$$

where a and b are the stoichiometric coefficients of A and B, $[A]$ and $[B]$ are the concentrations (usually the molarities) of A and B, and k is the reaction rate constant. Eq 1 includes the material balance condition for the chemical reaction, which, upon integration, becomes

$$\frac{[A] - [A]_0}{a} = \frac{[B] - [B]_0}{b} \quad (2)$$

where $[A]_0$ and $[B]_0$ are the zero-time concentrations of A and B. Text-book solutions (see, for example, Levine¹ or Atkins²) of this rate law are invariably based on the elimination of $[B]$ from eqs 1 and 2, followed by a rather complicated integration by partial fractions.

The purpose of this paper is to indicate a far simpler procedure by which eq 1 may be integrated. Two forms of this simplified integration will be presented. Both are based on re-arranging the material balance condition to give

$$b[A] - a[B] = b[A]_o - a[B]_o = C \quad (3)$$

and the observation that although $[A]$ and $[B]$ vary with time,

$C = b[A] - a[B]$ is a constant.

Method 1 : The first method of integration involves using both of the variables $[A]$ and $[B]$, rather than eliminating one of them. From the first and third members of eq 1 it follows that

$$\frac{d[A]}{[A]} = -ak[B]dt \quad (4)$$

Similarly, from the second and third members of eq 1

$$\frac{d[B]}{[B]} = -bk[A]dt \quad (5)$$

Subtracting eq 5 from eq 4 then yields

$$\frac{d[A]}{[A]} - \frac{d[B]}{[B]} = k(b[A] - a[B])dt \quad (6)$$

which, from the form of the material balance condition in eq 3, becomes

$$\frac{d[A]}{[A]} - \frac{d[B]}{[B]} = kCdt \quad (7)$$

Eq 7 is easily integrated from zero time to a later time giving

$$\ln([A]/[A]_o) - \ln([B]/[B]_o) = kCt \quad (8)$$

This solution to eq 1 is more commonly written in the form

$$\ln\left(\frac{[A]/[B]}{[A]_o/[B]_o}\right) = kCt \quad (9)$$

Method 2 : The second method involves using the concentration ratio $X = [A]/[B]$, rather than either of the concentrations $[A]$ or $[B]$. From eq 3

$$[A] = \frac{a[B] + C}{b} \quad (10)$$

Thus, it follows that

$$X = \frac{[A]}{[B]} = \frac{a}{b} + \frac{C}{b[B]} \quad (11)$$

Differentiating eq 11 then gives

$$\frac{dX}{dt} = - \frac{C}{[B]^2} \frac{d[B]}{dt} \quad (12)$$

Substituting eq 1 into eq 12 then yields

$$\frac{dX}{dt} = \frac{C}{[B]^2} k[A][B] = kCX \quad (13)$$

Thus, this second order reaction follows "first-order kinetics" in the ratio X . The rate equation is again easily integrated to provide

$$\ln(X/X_0) = kCt \quad (14)$$

which is equivalent to eq 9.

In conclusion, then, the integration of the rate law for a reaction which is first order in each of two reactants can be performed using calculus which is no more complicated than that employed in simple first-order reactions.

Literature Cited

1. Levine, I.N., Physical Chemistry, 3rd ed.; McGraw Hill: New York, 1988; pp 519-520.
2. Atkins, P.W., Physical Chemistry, 3rd ed.; Freeman: New York, 1986; p 695

